



Open porous foam oxide thermoelectric elements for hot gases and liquid environments

E. Sudhakar Reddy *, J.G. Noudem, C. Goupil

Crismat-Ensicaen, CNRT, CNRS-UMR 6508, 6 Bd Maréchal Juin, 14050 Caen Cedex, France

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Abstract

The development of open porous foams from a variety of substances such as polymers, metals and ceramics has led to many interesting applications of the porous structures. The large open porosity and high surface area of foams from oxide thermoelectric materials could also bring about new thermoelectric module designs. Currently, thermoelectric modules with bulk elements are mostly designed to extract waste heat from solid bodies for power generation. However, the majority of waste heat is generated in gaseous or liquid media. Foam structures could be an efficient solution to extract the waste heat from the hot gases and liquids as compared to their bulk counterparts. We detail the manufacturing of foams from oxide thermoelectric materials. Open porous foams of different porosities of *n* type thermoelectric $\text{Ca}_{0.95}\text{Sm}_{0.05}\text{MnO}_3$ material are fabricated as replicas of polyurethane foams. The foams are demonstrated as a thermoelectric generator in a simple module configuration with a butane flame torch as a heat source.

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1. Introduction

Thermoelectric materials are a class of substances that convert heat into electric power and vice versa. In any typical energy production or conversion process nearly fifty percent of the energy is wasted, mostly as heat. In the present state of diminishing natural energy resources, thermoelectric materials could play a significant role in their efficient utilization in conjunction with energy conversion processes. The solid state operation of thermoelectric modules with no movable mechanical parts will also make them highly reliable in their operation. Traditionally, thermoelectric modules are typically designed from bulk thermoelectric elements with flat ceramic plates for heat extraction and dissipation from the surface of solid bodies [1]. However, the source of waste heat from bulk bodies represents just a small portion of the waste heat, and mostly, the waste heat is in gaseous and liquid media. A

few examples are automobile exhausts, flames of household stoves, water boilers, hot springs, liquid metals in metallurgical factories etc. The direct extraction of heat from gaseous and liquid media by thermoelectric elements will be more efficient than heating a solid body and extracting the heat indirectly.

Foam materials are emerging as a distinct class in the categories of bulks, thick films and thin films with specific and promising applications in many areas [2,3]. Polymer foams have entered everyday life and are used for a host of purposes. Metallic foams are commercially available, under different trade names, for a variety of applications [3]. Most ceramic foams are used for standard applications such as filters or catalysts. The foam structures of advanced functional materials such as piezoelectric materials are rapidly evolving, allowing the tailoring of various physical properties [4]. Recently, foams of superconducting ceramic materials have been developed to provide critical solutions in applications, for reducing hot spot formation and decreasing thermal inertia [5]. Developing open porous foam structures of thermoelectric materials can result in

* Corresponding author. Tel.: +91 80 25032106; fax: +91 80 28412111.
E-mail address: [E.S. Reddy](mailto:E.SudhakarReddy@gmail.com).

designing efficient thermoelectric modules for waste heat sources involving gaseous and liquid media. Conventionally, thermoelectric modules were designed based on traditional materials such as Bi_2Te_3 , PbTe , SiGe etc. [6,7] in bulk form. The poor chemical stability and brittle nature of these materials has limited the processing of foam structures and designing modules using them. Also, the uses of these materials are limited to low temperatures, typically less than 300 °C. The recent development of high Seebeck coefficient thermoelectric oxide materials has opened opportunities to work with foam structures. Generally, the oxides are chemically stable and can be used at higher temperatures, even exceeding 1000 °C. The possibility of direct large area physical contact of thermoelectric foam elements with hot media will make them efficient electric power generators.

In this article, we demonstrate the fabrication of oxide open porous thermoelectric foams based on standard ceramic foam processing methods. Oxide material of *n* type thermoelectric $\text{Ca}_{0.95}\text{Sm}_{0.05}\text{MnO}_3$ is used as an example of processing open porous foams as replicas of polyurethane foams. A 100 pores per inch (PPI) oxide foam is used for demonstrating it as a thermoelectric generator in a simple module configuration with butane flame torch as heat source.

2. Preparation of thermoelectric foam

The *n* type thermoelectric $\text{Ca}_{0.95}\text{Sm}_{0.05}\text{MnO}_3$ (CSMO) foams of various porosities were produced as replicas of reticulated polyurethane foams. The use of polyurethane foams in processing ceramic foam replicas is well known in the ceramic foam industry. Although the use of polyurethane foam is common for ceramic foam manufacturing, the actual fabrication process is specific to the composition of the material. The choice of binders and plasticizers to result in the required viscosity of the slurry and the thermal schedules for burning out binders and sintering the oxide material are important factors. The CSMO powder used to prepare the slurries is processed by a standard solid state preparation route from the required amounts of high purity, CaCO_3 , Sm_2O_3 and Mn_2O_3 . The weighed stoichiometric powders of a total 150 g batch were mixed in a ball mill for 2 h in ethanol followed by drying at ambient temperatures. The dried powders, placed in alumina crucibles, were heated at a rate of 100 °C/h and fired for 24 h at 1050 °C. The annealed powders were further milled using zirconia balls to reduce the particle size to around a micron in agate ceramic pots placed on a centrifuge mill.

The slurry for impregnation of the polyurethane foams was prepared by mixing the CSMO powder in water with 4 wt% polyvinylalcohol as binder. It needs to be mentioned that the CSMO powder is chemically stable towards water, allowing us to work with water-based slurries. The water content in the slurry is adjusted to be in the range of 20 wt%. Commercially available polyurethane foams of 10 and 100 PPI (porosity) were used to pre-

pare thermoelectric oxide foams. The polyurethane foams were impregnated with thick oxide coatings by repeated dipping into the slurry with intermediate room temperature dryings. The dried PUC (polyurethane ceramic) foams with CSMO coatings were heated in a box type furnace in the ambient atmosphere to burn out the polymer and further sinter the oxide material. The binders and polyurethane are burned by slow heating at a rate of 50 °C/h to 600 °C. A further heating to 1350 °C at 100 °C/h and dwelling for 24 h resulted in densification of the oxide powders into a structural replica of the PUC foam. Fig. 1 shows the photographs of as-processed thermoelectric foams of different porosities. The thickness of the struts is calculated to be less than 100 μm, and the relative density is around 20% in the case of 100 PPI porosity foam with respect to its bulk counterpart. The fractured surface of the foams, Fig. 2, reveals the dense microstructure of the struts with average grain size of 3 μm. The X-ray diffraction pattern of the

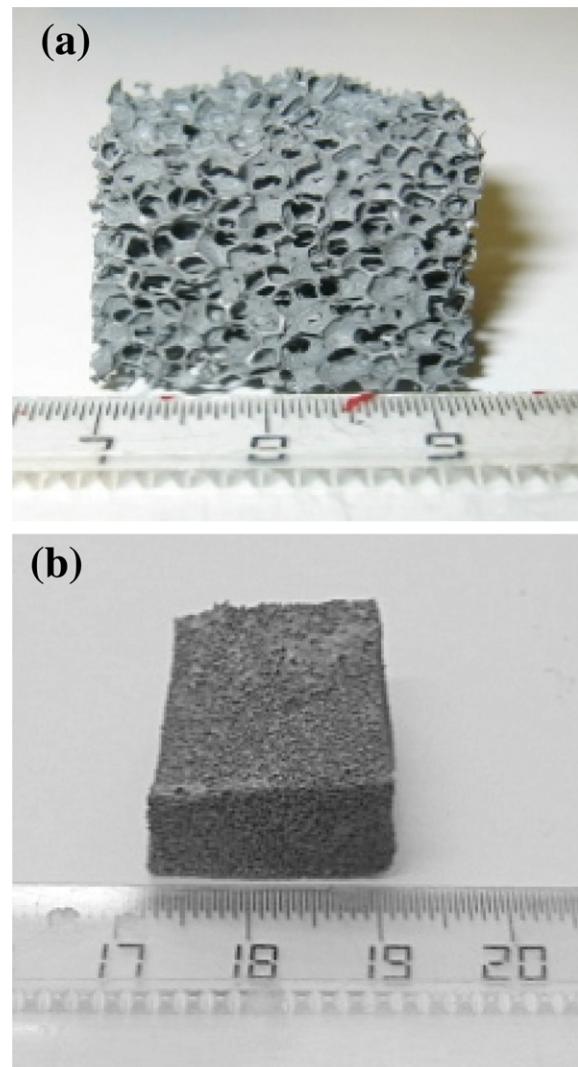


Fig. 1. Thermoelectric $\text{Ca}_{0.95}\text{Sm}_{0.05}\text{MnO}_3$ material processed as open porous foams replica of polyurethane foams with porosities of (a) 40 PPI (b) 100 PPI.

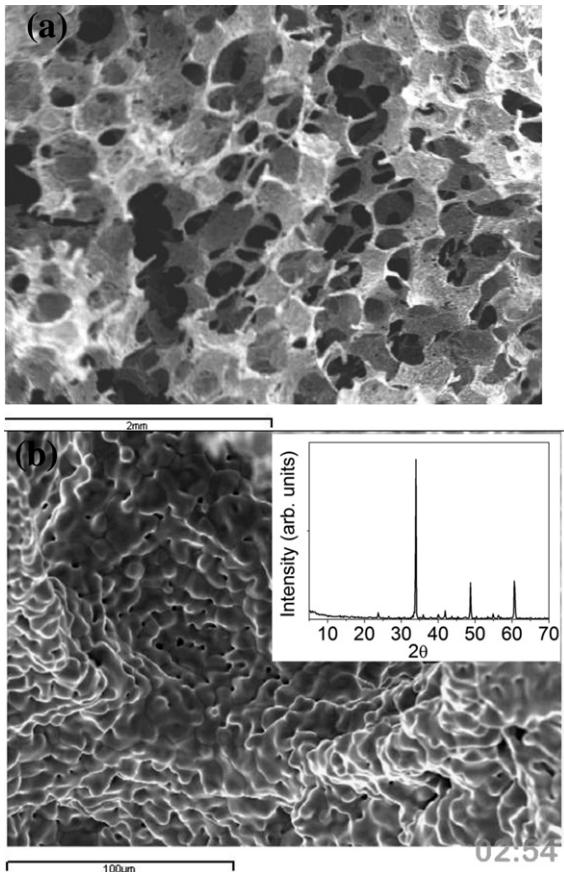


Fig. 2. SEM microstructure of a fractured surface of a 100 PPI thermoelectric foam. The dense structure of the struts can be noticed in (b). The inset shows the XRD pattern of the powdered $\text{Ca}_{0.95}\text{Sm}_{0.05}\text{MnO}_3$ foam.

powdered foam taken with Cu K α radiation is shown in Fig. 2. All peaks were indexed for the $\text{Ca}_{0.95}\text{Sm}_{0.05}\text{MnO}_3$ phase with no presence of impurities. The EDAX (energy dispersive X-ray microanalysis) chemical analysis also indicated no traces of carbon residue from the organics used for preparation of the thermoelectric foams.

3. Demonstration of thermoelectric generator

The ability of the oxide foam structures as thermoelectric generators is demonstrated in a simple configuration as shown schematically in Fig. 3a. A 100 PPI foam of $30 \times 10 \times 10 \text{ mm}^3$ was used for the experiment. The electrical contacts for the oxide foams were made by coating silver paint up to around 2 mm length, Fig. 3b, on both ends and metalising at 935°C for 5 h. The performance is evaluated by heating one end of the foam by a butane + propane flame torch and simultaneously recording various parameters, viz. temperatures along the length of the foam, open circuit current and voltage, internal resistance and Seebeck coefficients by an automated Keithley K2700/7700 scanning system and a computer. Temperature gradients of around 500°C were created along the length of the thermoelectric foam by heating one end of the foam to

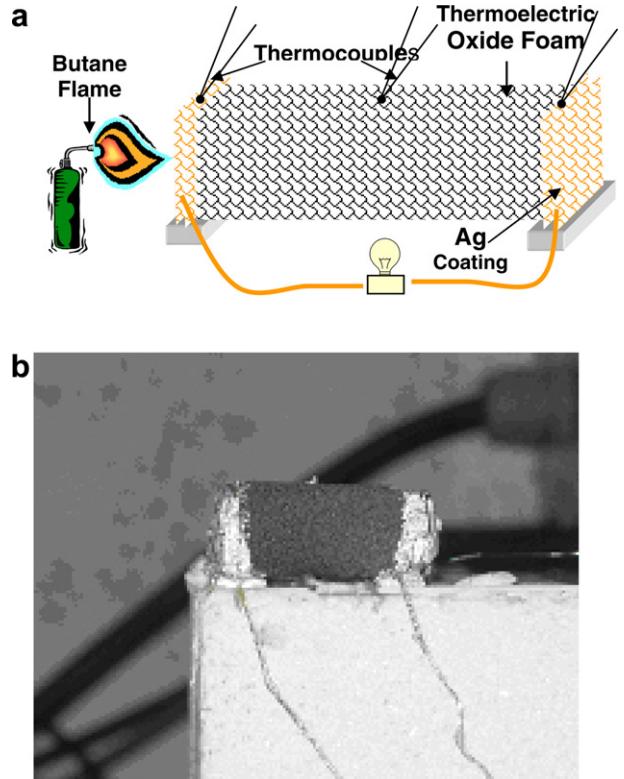


Fig. 3. Schematic diagram illustrating the configuration used to evaluate the thermoelectric foam as a thermoelectric generator. The heat source used is a butane + propane flame torch. The inset shows a 100 PPI $\text{Ca}_{0.95}\text{Sm}_{0.05}\text{MnO}_3$ foam fabricated accordingly. The electrical contacts, at the ends of the foam, are fabricated by painting silver paste and metallising at 935°C .

575°C and placing the other end in ambient air. The temperatures recorded, by three k thermocouples, along the length of the foam in a typical run is shown in Fig. 4. The Seebeck coefficient, directly measured on the foam,

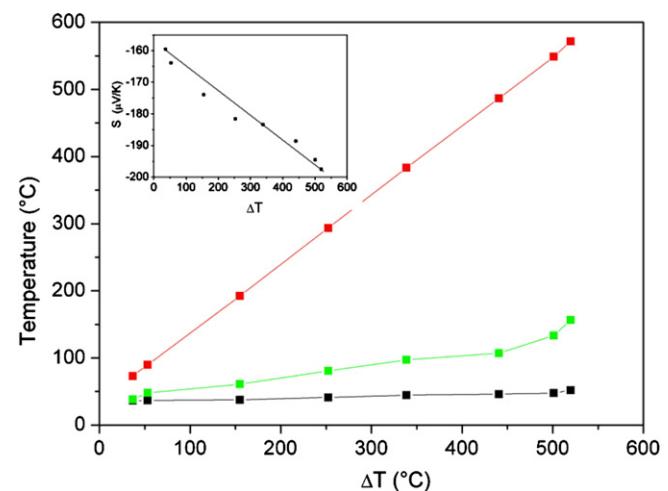


Fig. 4. The measured temperatures along the length of the foam. The inset shows the Seebeck coefficient of the foam. The fluctuations in the values are due to the inability to maintain precise temperature stability along the length of the foam due to the nature of the heat source, flame torch, used.

Table 1

Various physical parameters measured for the thermoelectric foam module at 575 °C

| Module type | T_{hot} (°C) | ΔT (°C) | $\langle \alpha_n \rangle$ ($\mu\text{V/K}$) | R (Ω) | E_0 (mV) | P_{max} (mW) |
|-------------|-----------------------|-----------------|------------------------------------------------|------------------|------------|-----------------------|
| Foam | 575 | 500 | -197 | 12.5 | 100 | 1 |

when working in an open circuit mode, is shown as an inset in Fig. 4. The various parameters recorded are summarized in Table 1. An open circuit voltage of 100 mV was generated at an operation temperature of 575 °C with 500 °C gradient and internal resistance of 12 Ω. A maximum output power of 1 mW was obtained.

4. Outlook

The outlook for oxide foam structures is quite promising. The availability of thermoelectric foams could result in designing unique and efficient thermoelectric modules for specific heat source environments. The oxide thermoelectric foams are also of interest to replace bulk thermoelectric elements in conventional module designs. Basically, the efficiency of the thermoelectric materials is an interplay between the electrical and thermal conductivities. The dimensionless efficiency factor is given by $ZT = S^2\sigma/\kappa$, where S is the Seebeck coefficient, and σ and κ are the electrical and thermal conductivities, respectively. Foams are well known to have very different effective properties than their bulk counterparts [8–10]. At high porosities, exceeding 90%, various theoretical models, such as the tetrakiadecahedron and cube models [8,10], indicate that the effective rate of increase in electrical conductivity is more than that in thermal conductivity. Finding an optimal porosity with increased ratio of the electrical to thermal conductivities for a given thermoelectric foam element could result in increasing the ZT and, hence, the efficiency of the thermoelectric generator.

Another advantage of the foam structure is that the large surface area of foams could result in fabricating low ohmic electrical contacts to the thermoelectric materials.

5. Conclusion

In conclusion, the manufacturing of foams from oxide thermoelectric materials and the concept of using foam structures to extract waste heats from gaseous and liquid environments have been discussed. The high surface area of the foams allows an efficient heat extraction as compared to bulk materials. The thermoelectric $\text{Ca}_{0.95}\text{Sm}_{0.05}\text{MnO}$ material has been processed as a replica of polyurethane foams and demonstrated as a thermoelectric generator. In a simple thermoelectric module configuration, with butane torch flame as the heat source, a 100 PPI foam is observed to have an open circuit voltage of 100 mV at 575 °C and applied temperature gradient of 500 °C.

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